

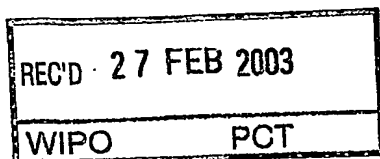
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10/500918 21.02.03



INVESTOR IN PEOPLE



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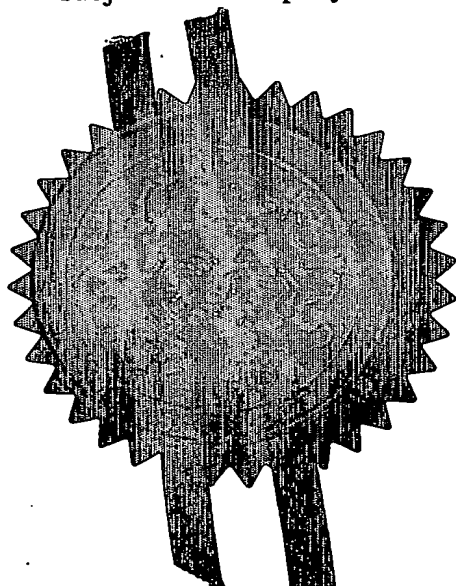
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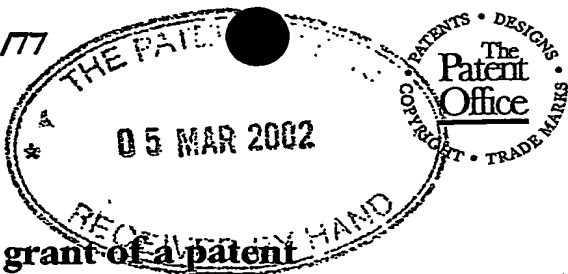
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# Request for grant of a patent

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Cardiff Road  
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NP10 8QQ

1. Your reference

PPD 50701/GB/P

2. Patent application number

(The Patent Office)

0205127.4

5 MAR 2002

3. 1. Name of the applicant (underline all surnames)

SYNGENTA Participations AG  
Intellectual Property Department  
Schwarzwaldallee 215  
CH-4058 Basel  
SWITZERLAND

Patents ADP number (if you know it)

8029555001

If the applicant is a corporate body, give the country/state of its incorporation

SWITZERLAND

4. Title of the invention

CHEMICAL COMPOUNDS

5. Name of your agent (if you have one)

Martin Keith Osborn  
Intellectual Property Department  
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PO Box 3538  
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UNITED KINGDOM

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Patents ADP number (if you know it)

8019945002

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

Priority application number  
(if you know it)

Date of filing  
(day / month / year)

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing  
(day / month / year)

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

- a) any applicant named in part 3 is not an inventor, or
  - b) there is an inventor who is not named as an applicant, or
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Description 27

Claim(s) 02

Abstract 01

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Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (Patents Form 7/77)

Request for preliminary examination and search (Patents Form 9/77)

Request for substantive examination (Patents Form 10/77)

Any other documents (please specify)

11.

I/We request the grant of a patent on the basis of this application.  
Syngenta Participations AG

Signature *Joanna Chandler*  
Authorised Signatory

Date 5/3/02

12. Name and daytime telephone number of person to contact in the United Kingdom

Joanna Carmen CHANDLER = 01344 414365

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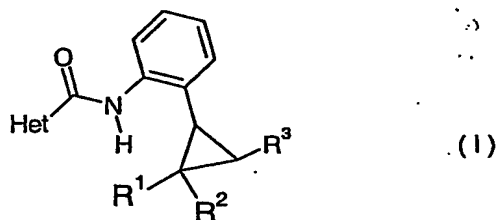
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CHEMICAL COMPOUNDS

The present invention relates to novel ortho-cyclopropyl-azol-carboxamides which have microbiocidal activity, in particular fungicidal activity. The invention also relates to the preparation of these compounds, to novel intermediates used in the preparation of these compounds, to agrochemical compositions which comprise at least one of the novel compounds as active ingredient, to the preparation of the compositions mentioned and to the use of the active ingredients or compositions in agriculture or horticulture for controlling or preventing infestation of plants by phytopathogenic microorganisms, preferably fungi.

The present invention provides a compound of formula (I):



where

Het is a 5- or 6-membered heterocyclic ring containing one to three heteroatoms, each independently selected from oxygen, nitrogen and sulphur, the ring being substituted by groups  $R^4$ ,  $R^5$  and  $R^6$ ;

$R^1$  is hydrogen or halo;

$R^2$  is hydrogen or halo;

$R^3$  is optionally substituted  $C_{2-12}$  alkyl, optionally substituted  $C_{2-12}$  alkenyl, optionally substituted  $C_{2-12}$  alkynyl, optionally substituted  $C_{3-12}$  cycloalkyl, optionally substituted phenyl or optionally substituted heterocyclyl; and

$R^4$ ,  $R^5$  and  $R^6$  are, independently, selected from hydrogen, halo, cyano, nitro,  $C_{1-4}$  alkyl,  $C_{1-4}$  haloalkyl,  $C_{1-4}$  alkoxy( $C_{1-4}$ )alkyl and  $C_{1-4}$  haloalkoxy( $C_{1-4}$ )alkyl, provided that at least one of  $R^4$ ,  $R^5$  and  $R^6$  is not hydrogen.

Halo is fluoro, chloro or bromo.

Each alkyl moiety is a straight or branched chain and is, for example, methyl, ethyl, *n*-propyl, *n*-butyl, *n*-pentyl, *n*-hexyl, *iso*-propyl, *n*-butyl, *sec*-butyl, *iso*-butyl, *tert*-butyl or *neo*-pentyl.

When present, each optional substituent on an alkyl moiety is, independently, selected from halo, hydroxy, cyano, C<sub>1-4</sub>alkoxyC(=O), formyl, nitro, C<sub>1-4</sub> alkoxy, C<sub>1-4</sub> haloalkoxy, C<sub>1-4</sub> alkylthio, C<sub>1-4</sub> haloalkylthio, HC(OR')=N and R'R''NN=C(H); where R' and R'' are, independently, hydrogen or C<sub>1-4</sub> alkyl.

5 Alkenyl and alkynyl moieties can be in the form of straight or branched chains. The alkenyl moieties, where appropriate, can be of either the (E)- or (Z)-configuration. Examples are vinyl, allyl and propargyl.

When present, each optional substituent on alkenyl or on alkynyl is, independently, selected from those optional substituents given above for an alkyl moiety.

10 Cycloalkyl includes cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl.

When present, each optional substituent on cycloalkyl is, independently, selected from C<sub>1-3</sub> alkyl and those optional substituents given above for an alkyl moiety.

The term heterocyclyl refers to a non-aromatic or aromatic ring containing up to 10 atoms including one or more (preferably one or two) heteroatoms selected, each 15 independently, from O, S and N. Examples of such rings include 1,3-dioxolanyl, tetrahydrofuranyl, morpholinyl, thienyl and furyl.

When present, each optional substituent on phenyl or on heterocyclyl is, independently, selected from C<sub>1-6</sub> alkyl and those optional substituents given above for an alkyl moiety. When present, there are up to four optional substituents on phenyl, each 20 independently selected.

When present, each optional substituent on an alkyl moiety is, independently, selected from the preferred list of halo, hydroxy, methoxy, trifluoromethoxy, difluoromethoxy, cyano and nitro.

When present, each optional substituent on alkenyl or on alkynyl is, independently, 25 selected from the preferred list of halo and cyano.

When present, each optional substituent on cycloalkyl is, independently, selected from the preferred list of methyl, ethyl, trifluoromethyl, methoxy, trifluoromethoxy and cyano.

When present, each optional substituent on phenyl or on a heterocyclyl group is, 30 independently, selected from the preferred list of halo, hydroxy, methoxy, trifluoromethoxy, difluoromethoxy and cyano.

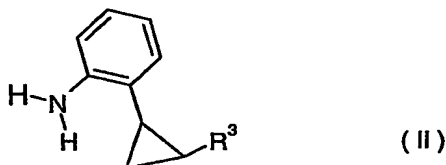
It is preferred that Het is pyrrolyl, pyrazolyl, thiazolyl, pyridinyl, pyrimidinyl, thiophenyl, furyl, isothiazolyl or isoxazolyl (more preferably pyrrolyl, pyrazolyl or thiazolyl), each being substituted by groups  $R^4$ ,  $R^5$  and  $R^6$ .

Preferably  $R^1$  and  $R^2$  are, independently, hydrogen or fluoro.

5 Preferably  $R^3$  is  $C_{2-6}$  alkyl, optionally substituted  $C_{3-8}$  cycloalkyl, phenyl, thienyl or furyl.

Preferably  $R^4$ ,  $R^5$  and  $R^6$  are, independently, selected from hydrogen, halogen,  $C_{1-4}$  alkyl,  $C_{1-4}$  haloalkyl and  $C_{1-4}$  alkoxy( $C_{1-4}$ )alkyl, provided that at least one of  $R^4$ ,  $R^5$  and  $R^6$  is not hydrogen. More preferably  $R^4$ ,  $R^5$  and  $R^6$  are, independently, selected from  
10 hydrogen, halogen, methyl,  $C_{1-2}$  haloalkyl and methoxymethyl, provided that at least one of  $R^4$ ,  $R^5$  and  $R^6$  is not hydrogen.

Compounds of formula (II):



where  $R^3$  is as defined above for a compound of formula (I), are also novel and are  
15 useful as intermediates in the preparation of compounds of formula (I).

Therefore, in another aspect the present invention provides a compound of formula (II) where  $R^3$  is as defined above for a compound of formula (I).

The compounds of formula (I) and of formula (II) may exist as different  
geometric or optical isomers or in different tautomeric forms. This invention covers all  
20 such isomers and tautomers and mixtures thereof in all proportions as well as isotopic forms such as deuterated compounds.

The compounds in Tables 1 to 6 below illustrate compounds of the invention.

Table 1 provides 22 compounds of formula (II) wherein  $R^3$  is as defined in Table

1.

Table 1

Compound Number	R <sup>3</sup>
1.1	CH <sub>2</sub> CH <sub>3</sub>
1.2	CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>
1.3	CH(CH <sub>3</sub> ) <sub>2</sub>
1.4	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>
1.5	CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>
1.6	C(CH <sub>3</sub> ) <sub>3</sub>
1.7	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>
1.8	CH <sub>2</sub> CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>
1.9	CH <sub>2</sub> CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>
1.10	cyclopropyl
1.11	cyclobutyl
1.12	cyclopentyl
1.13	cyclohexyl
1.14	cycloheptyl
1.15	cyclooctyl
1.16	phenyl
1.17	p-Cl-phenyl
1.18	p-F-phenyl
1.19	p-Br-phenyl
1.20	thienyl
1.21	furyl
1.22	α-methylcyclopropyl

Table X

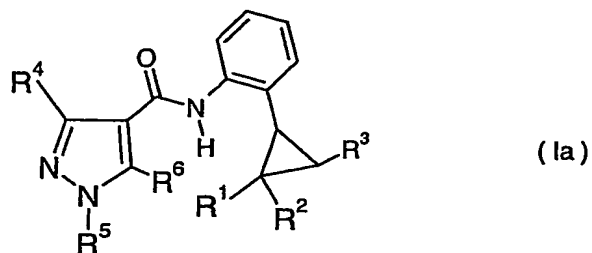
Compound Number	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	R <sup>5</sup>	R <sup>6</sup>
X.1	H	H	CH <sub>2</sub> CH <sub>3</sub>	CF <sub>3</sub>	CH <sub>3</sub>	H
X.2	H	H	CH <sub>2</sub> CH <sub>3</sub>	CF <sub>3</sub>	CH <sub>2</sub> OCH <sub>3</sub>	H
X.3	H	H	CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	CF <sub>3</sub>	CH <sub>3</sub>	H
X.4	H	H	CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	CF <sub>2</sub> H	CH <sub>3</sub>	H
X.5	H	H	CH(CH <sub>3</sub> ) <sub>2</sub>	CF <sub>3</sub>	CH <sub>3</sub>	H
X.6	H	H	CH(CH <sub>3</sub> ) <sub>2</sub>	CF <sub>2</sub> H	CH <sub>3</sub>	H
X.7	H	H	CH(CH <sub>3</sub> ) <sub>2</sub>	CFH <sub>2</sub>	CH <sub>3</sub>	H
X.8	H	H	CH(CH <sub>3</sub> ) <sub>2</sub>	CH <sub>3</sub>	CH <sub>3</sub>	Cl
X.9	H	H	CH(CH <sub>3</sub> ) <sub>2</sub>	CH <sub>3</sub>	CH <sub>2</sub> CH <sub>3</sub>	Cl
X.10	H	H	CH(CH <sub>3</sub> ) <sub>2</sub>	CH <sub>3</sub>	CH <sub>3</sub>	F
X.11	H	H	CH(CH <sub>3</sub> ) <sub>2</sub>	CH <sub>3</sub>	CH <sub>2</sub> CH <sub>3</sub>	F
X.12	H	H	CH(CH <sub>3</sub> ) <sub>2</sub>	CF <sub>2</sub> Cl	CH <sub>3</sub>	F
X.13	H	H	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	CF <sub>3</sub>	CH <sub>3</sub>	H
X.14	H	H	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	CF <sub>2</sub> H	CH <sub>3</sub>	H
X.15	H	H	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	F
X.16	H	H	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	Cl
X.17	H	H	CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	CF <sub>3</sub>	CH <sub>3</sub>	H
X.18	H	H	CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	CF <sub>2</sub> H	CH <sub>3</sub>	H
X.19	H	H	CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	CFH <sub>2</sub>	CH <sub>3</sub>	H
X.20	H	H	CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	CF <sub>3</sub>	CH <sub>2</sub> OCH <sub>3</sub>	H
X.21	H	H	CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	CH <sub>3</sub>	CH <sub>3</sub>	F
X.22	H	H	CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	CH <sub>3</sub>	CH <sub>3</sub>	Cl
X.23	H	H	C(CH <sub>3</sub> ) <sub>3</sub>	CF <sub>3</sub>	CH <sub>3</sub>	H
X.24	H	H	C(CH <sub>3</sub> ) <sub>3</sub>	CF <sub>2</sub> H	CH <sub>3</sub>	H
X.25	H	H	C(CH <sub>3</sub> ) <sub>3</sub>	CF <sub>2</sub> H	CH <sub>3</sub>	H
X.26	H	H	C(CH <sub>3</sub> ) <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	F
X.27	H	H	C(CH <sub>3</sub> ) <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	Cl
X.28	H	H	C(CH <sub>3</sub> ) <sub>3</sub>	CF <sub>2</sub> Cl	CH <sub>3</sub>	H



Compound Number	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	R <sup>5</sup>	R <sup>6</sup>
X.29	H	H	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	CF <sub>3</sub>	CH <sub>3</sub>	H
X.30	H	H	CH <sub>2</sub> CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	CF <sub>3</sub>	CH <sub>3</sub>	H
X.31	H	H	CH <sub>2</sub> CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	CF <sub>2</sub> H	CH <sub>3</sub>	H
X.32	H	H	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	CF <sub>3</sub>	CH <sub>3</sub>	H
X.33	H	H	cyclopropyl	CF <sub>3</sub>	CH <sub>3</sub>	H
X.34	H	H	cyclopropyl	CF <sub>2</sub> H	CH <sub>3</sub>	H
X.35	H	H	cyclopropyl	CH <sub>3</sub>	CH <sub>3</sub>	F
X.36	H	H	cyclopropyl	CH <sub>3</sub>	CH <sub>3</sub>	Cl
X.37	H	H	cyclobutyl	CF <sub>3</sub>	CH <sub>3</sub>	H
X.38	H	H	cyclobutyl	CF <sub>2</sub> H	CH <sub>3</sub>	H
X.39	H	H	cyclopentyl	CF <sub>3</sub>	CH <sub>3</sub>	H
X.40	H	H	cyclopentyl	CF <sub>2</sub> H	CH <sub>3</sub>	H
X.41	H	H	cyclopentyl	CFH <sub>2</sub>	CH <sub>3</sub>	H
X.42	H	H	cyclopentyl	CF <sub>2</sub> Cl	CH <sub>3</sub>	H
X.43	H	H	cyclopentyl	CH <sub>3</sub>	CH <sub>3</sub>	F
X.44	H	H	cyclopentyl	CH <sub>3</sub>	CH <sub>3</sub>	Cl
X.45	H	H	cyclopentyl	CF <sub>3</sub>	CH <sub>3</sub>	H
X.46	H	H	cyclopentyl	CF <sub>2</sub> H	CH <sub>3</sub>	H
X.47	H	H	cyclopentyl	CFH <sub>2</sub>	CH <sub>3</sub>	H
X.48	H	H	cyclopentyl	CF <sub>2</sub> Cl	CH <sub>3</sub>	H
X.49	F	F	cyclopentyl	CF <sub>3</sub>	CH <sub>3</sub>	H
X.50	H	H	cyclopentyl	CH <sub>3</sub>	CH <sub>3</sub>	F
X.51	H	H	cyclopentyl	CH <sub>3</sub>	CH <sub>3</sub>	Cl
X.52	H	H	cyclopentyl	CF <sub>3</sub>	CH <sub>3</sub>	H
X.53	H	H	cyclopentyl	CF <sub>3</sub>	CH <sub>2</sub> CH <sub>3</sub>	H
X.54	H	H	cyclopentyl	CF <sub>2</sub> H	CH <sub>3</sub>	H
X.55	H	H	cyclopentyl	CFH <sub>2</sub>	CH <sub>3</sub>	H
X.56	H	H	cyclopentyl	CF <sub>2</sub> Cl	CH <sub>3</sub>	F
X.57	H	H	cyclopentyl	CH <sub>3</sub>	CH <sub>3</sub>	F

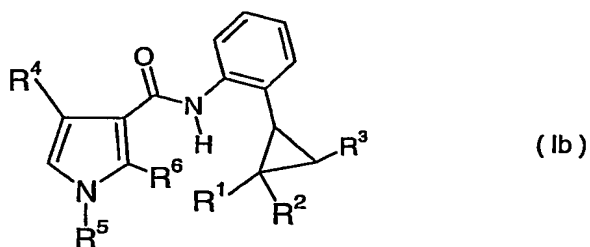
Compound Number	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	R <sup>5</sup>	R <sup>6</sup>
X.57	H	H	cyclopentyl	CH <sub>3</sub>	CH <sub>3</sub>	F
X.58	H	H	cyclopentyl	CH <sub>3</sub>	CH <sub>3</sub>	Cl
X.59	H	H	cyclopentyl	CF <sub>3</sub>	CH <sub>3</sub>	H
X.60	H	H	cyclopentyl	CF <sub>2</sub> H	CH <sub>3</sub>	H
X.61	H	H	phenyl	CF <sub>3</sub>	CH <sub>3</sub>	H
X.62	H	H	phenyl	CF <sub>2</sub> H	CH <sub>3</sub>	H
X.63	H	H	phenyl	CFH <sub>2</sub>	CH <sub>3</sub>	H
X.64	H	H	phenyl	CH <sub>3</sub>	CH <sub>3</sub>	F
X.65	H	H	phenyl	CH <sub>3</sub>	CH <sub>3</sub>	Cl
X.66	H	H	4-fluorophenyl	CF <sub>3</sub>	CH <sub>3</sub>	H
X.67	H	H	4-fluorophenyl	CF <sub>2</sub> H	CH <sub>3</sub>	H
X.68	H	H	4-chlorophenyl	CF <sub>3</sub>	CH <sub>3</sub>	H
X.69	H	H	4-chlorophenyl	CF <sub>2</sub> H	CH <sub>3</sub>	H
X.70	H	H	4-bromophenyl	CF <sub>3</sub>	CH <sub>3</sub>	H
X.71	H	H	4-bromophenyl	CF <sub>2</sub> H	CH <sub>3</sub>	H
X.72	H	H	2-thienyl	CF <sub>3</sub>	CH <sub>3</sub>	H
X.73	H	H	3-thienyl	CF <sub>3</sub>	CH <sub>3</sub>	H
X.74	H	H	2-furyl	CF <sub>3</sub>	CH <sub>3</sub>	H
X.75	H	H	2-furyl	CF <sub>3</sub>	CH <sub>3</sub>	H
X.76	H	H	$\alpha$ -methylcyclopropyl	CF <sub>3</sub>	CH <sub>3</sub>	H
X.77	H	H	$\alpha$ -methylcyclopropyl	CF <sub>2</sub> H	CH <sub>3</sub>	H
X.78	H	H	$\alpha$ -methylcyclopropyl	CH <sub>3</sub>	CH <sub>3</sub>	F
X.79	H	H	$\alpha$ -methylcyclopropyl	CH <sub>3</sub>	CH <sub>3</sub>	Cl

Table 2 provides 79 compounds of formula (1a):



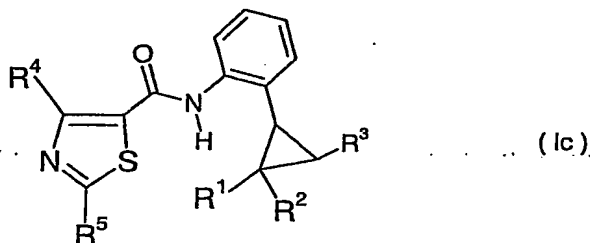
wherein  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$  and  $R^6$  are as defined in Table 2.

Table 3 provides 79 compounds of formula (1b):



wherein  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$  and  $R^6$  are as defined in Table 3.

Table 4 provides 50 compounds of formula (1c):



wherein  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$  and  $R^5$  are as defined in Table 4.

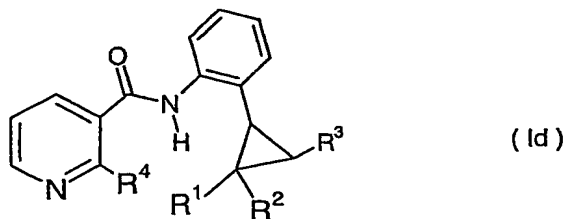
Table 4

Compound Number	$R^1$	$R^2$	$R^3$	$R^4$	$R^5$
4.1	H	H	$\text{CH}_2\text{CH}_3$	$\text{CF}_3$	$\text{CH}_3$
4.2	H	H	$\text{CH}_2\text{CH}_3$	$\text{CH}_3$	$\text{CH}_3$
4.3	H	H	$\text{CH}_2\text{CH}_2\text{CH}_3$	$\text{CF}_3$	$\text{CH}_3$
4.4	H	H	$\text{CH}_2\text{CH}_2\text{CH}_3$	$\text{CH}_3$	$\text{CH}_3$

Compound Number	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	R <sup>5</sup>
4.5	H	H	CH(CH <sub>3</sub> ) <sub>2</sub>	CF <sub>3</sub>	CH <sub>3</sub>
4.6	H	H	CH(CH <sub>3</sub> ) <sub>2</sub>	CH <sub>3</sub>	CH <sub>3</sub>
4.7	H	H	CH(CH <sub>3</sub> ) <sub>2</sub>	CH <sub>2</sub> CH <sub>3</sub>	CH <sub>3</sub>
4.8	H	H	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	CF <sub>3</sub>	CH <sub>3</sub>
4.9	H	H	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>
4.10	H	H	CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	CF <sub>3</sub>	CH <sub>3</sub>
4.11	H	H	CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	CH <sub>3</sub>	CH <sub>3</sub>
4.12	H	H	C(CH <sub>3</sub> ) <sub>3</sub>	CF <sub>3</sub>	CH <sub>3</sub>
4.13	H	H	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	CF <sub>3</sub>	CH <sub>3</sub>
4.14	H	H	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>
4.15	H	H	CH <sub>2</sub> CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	CF <sub>3</sub>	CH <sub>3</sub>
4.16	H	H	CH <sub>2</sub> CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	CH <sub>3</sub>	CH <sub>3</sub>
4.17	H	H	CH <sub>2</sub> CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	CH <sub>3</sub>	CH <sub>2</sub> CH <sub>3</sub>
4.18	H	H	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	CF <sub>3</sub>	CH <sub>3</sub>
4.19	H	H	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>
4.20	H	H	cyclopropyl	CF <sub>3</sub>	CH <sub>3</sub>
4.21	H	H	cyclopropyl	CH <sub>3</sub>	CH <sub>3</sub>
4.22	H	H	cyclobutyl	CF <sub>3</sub>	CH <sub>3</sub>
4.23	H	H	cyclobutyl	CH <sub>3</sub>	CH <sub>3</sub>
4.24	H	H	cyclopentyl	CF <sub>3</sub>	CH <sub>3</sub>
4.25	H	H	cyclopentyl	CH <sub>3</sub>	CH <sub>3</sub>
4.26	H	H	cyclopentyl	CF <sub>3</sub>	CH <sub>3</sub>
4.27	H	H	cyclopentyl	CH <sub>3</sub>	CH <sub>3</sub>
4.28	F	F	cyclopentyl	CF <sub>3</sub>	CH <sub>3</sub>
4.29	H	H	cycloheptyl	CF <sub>3</sub>	CH <sub>3</sub>
4.30	H	H	cycloheptyl	CH <sub>3</sub>	CH <sub>3</sub>
4.31	H	H	cyclooctyl	CF <sub>3</sub>	CH <sub>3</sub>
4.32	H	H	cyclooctyl	CH <sub>3</sub>	CH <sub>3</sub>
4.33	H	H	phenyl	CF <sub>3</sub>	CH <sub>3</sub>

Compound Number	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	R <sup>5</sup>
4.34	H	H	phenyl	CH <sub>3</sub>	CH <sub>3</sub>
4.35	H	H	4-fluorophenyl	CF <sub>3</sub>	CH <sub>3</sub>
4.36	H	H	4-fluorophenyl	CH <sub>3</sub>	CH <sub>3</sub>
4.37	H	H	4-chlorophenyl	CF <sub>3</sub>	CH <sub>3</sub>
4.38	H	H	4-chlorophenyl	CF <sub>3</sub>	CH <sub>3</sub>
4.39	H	H	4-bromophenyl	CF <sub>3</sub>	CH <sub>3</sub>
4.40	H	H	4-bromophenyl	CH <sub>3</sub>	CH <sub>3</sub>
4.41	H	H	2-thienyl	CF <sub>3</sub>	CH <sub>3</sub>
4.42	H	H	2-thienyl	CH <sub>3</sub>	CH <sub>3</sub>
4.43	H	H	3-thienyl	CF <sub>3</sub>	CH <sub>3</sub>
4.44	H	H	3-thienyl	CH <sub>3</sub>	CH <sub>3</sub>
4.45	H	H	2-furyl	CF <sub>3</sub>	CH <sub>3</sub>
4.46	H	H	2-furyl	CH <sub>3</sub>	CH <sub>3</sub>
4.47	H	H	3-furyl	CF <sub>3</sub>	CH <sub>3</sub>
4.48	H	H	3-furyl	CH <sub>3</sub>	CH <sub>3</sub>
4.49	H	H	$\alpha$ -methylcyclopropyl	CF <sub>3</sub>	CH <sub>3</sub>
4.50	H	H	$\alpha$ -methylcyclopropyl	CH <sub>3</sub>	CH <sub>3</sub>

Table 5 provides 54 compounds of formula (1d):



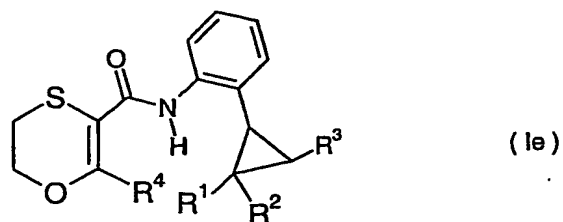
wherein R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are as defined in Table 5.

Table 5

Compound Number	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>
5.1	H	H	CH <sub>2</sub> CH <sub>3</sub>	Cl
5.2	H	H	CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	Cl
5.3	H	H	CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	Br
5.4	H	H	CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	CF <sub>3</sub>
5.5	H	H	CH(CH <sub>3</sub> ) <sub>2</sub>	Cl
5.6	H	H	CH(CH <sub>3</sub> ) <sub>2</sub>	Br
5.7	H	H	CH(CH <sub>3</sub> ) <sub>2</sub>	CF <sub>3</sub>
5.8	H	H	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	Cl
5.9	H	H	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	Br
5.10	H	H	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	CF <sub>3</sub>
5.11	H	H	C(CH <sub>3</sub> ) <sub>3</sub>	Cl
5.12	H	H	CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	Cl
5.13	H	H	CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	Br
5.14	H	H	CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	CF <sub>3</sub>
5.15	H	H	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	Cl
5.16	H	H	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	Br
5.17	H	H	CH <sub>2</sub> CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	Cl
5.18	H	H	CH <sub>2</sub> CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	Br
5.19	H	H	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	Cl
5.20	H	H	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	Br
5.21	H	H	cyclopropyl	Cl
5.22	H	H	cyclopropyl	Br
5.23	H	H	cyclobutyl	Cl
5.24	H	H	cyclobutyl	Br
5.25	H	H	cyclopentyl	Cl
5.26	H	H	cyclopentyl	Br
5.27	F	F	cyclopentyl	CF <sub>3</sub>
5.28	H	H	cyclohexyl	Cl

Compound Number	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>
5.29	H	H	cyclohexyl	Br
5.30	H	H	cyclohexyl	CF <sub>3</sub>
5.31	H	H	cycloheptyl	Cl
5.32	H	H	cycloheptyl	Br
5.33	H	H	cycloheptyl	CF <sub>3</sub>
5.34	H	H	cyclooctyl	Cl
5.35	H	H	phenyl	Cl
5.36	H	H	phenyl	Br
5.37	H	H	4-fluorophenyl	Cl
5.38	H	H	4-fluorophenyl	Br
5.39	H	H	4-fluorophenyl	CF <sub>3</sub>
5.40	H	H	4-chlorophenyl	Cl
5.41	H	H	4-chlorophenyl	Br
5.42	H	H	4-chlorophenyl	CF <sub>3</sub>
5.43	H	H	4-bromophenyl	Cl
5.44	H	H	2-thienyl	Cl
5.45	H	H	2-thienyl	Br
5.46	H	H	3-thienyl	Cl
5.47	H	H	3-thienyl	Cl
5.48	H	H	2-furyl	Cl
5.49	H	H	2-furyl	Br
5.50	H	H	3-furyl	Cl
5.51	H	H	3-furyl	Br
5.52	H	H	2-pyridyl	Cl
5.53	H	H	$\alpha$ -methylcyclopropyl	Cl
5.54	H	H	$\alpha$ -methylcyclopropyl	Br

Table 6 provides 45 compounds of formula (1e):



wherein  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  are as defined in Table 6.

Table 6

Compound Number	$R^1$	$R^2$	$R^3$	$R^4$
6.1	H	H	$\text{CH}_2\text{CH}_3$	$\text{CH}_3$
6.2	H	H	$\text{CH}_2\text{CH}_2\text{CH}_3$	$\text{CF}_3$
6.3	H	H	$\text{CH}_2\text{CH}_2\text{CH}_3$	$\text{CH}_3$
6.4	H	H	$\text{CH}(\text{CH}_3)_2$	$\text{CF}_3$
6.5	H	H	$\text{CH}(\text{CH}_3)_2$	$\text{CH}_3$
6.6	H	H	$\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	$\text{CF}_3$
6.7	H	H	$\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	$\text{CH}_3$
6.8	H	H	$\text{CH}_2\text{CH}(\text{CH}_3)_2$	$\text{CF}_3$
6.9	H	H	$\text{CH}_2\text{CH}(\text{CH}_3)_2$	$\text{CH}_3$
6.10	H	H	$\text{C}(\text{CH}_3)_3$	$\text{CF}_3$
6.11	H	H	$\text{C}(\text{CH}_3)_3$	$\text{CH}_3$
6.12	H	H	$\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	$\text{CF}_3$
6.13	H	H	$\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	$\text{CH}_3$
6.14	H	H	$\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$	$\text{CF}_3$
6.15	H	H	$\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$	$\text{CH}_3$
6.16	H	H	$\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	$\text{CF}_3$
6.17	H	H	$\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	$\text{CH}_3$
6.18	H	H	cyclopropyl	$\text{CF}_3$
6.19	H	H	cyclopropyl	$\text{CH}_3$
6.20	H	H	cyclobutyl	$\text{CF}_3$
6.21	H	H	cyclobutyl	$\text{CH}_3$
6.22	H	H	cycloheptyl	$\text{CF}_3$



Compound Number	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>
6.23	H	H	cycloheptyl	CH <sub>3</sub>
6.24	H	H	cycloheptyl	CF <sub>3</sub>
6.25	H	H	Cyclopentyl	CH <sub>3</sub>
6.26	H	H	cyclopentyl	CF <sub>3</sub>
6.27	F	F	cycloheptyl	CH <sub>3</sub>
6.28	H	H	cycloodyl	CF <sub>3</sub>
6.29	H	H	phenyl	CF <sub>3</sub>
6.30	H	H	phenyl	CH <sub>3</sub>
6.31	H	H	4-fluorophenyl	CF <sub>3</sub>
6.32	H	H	4-flurophenyl	CH <sub>3</sub>
6.33	H	H	4-chlorophenyl	CF <sub>3</sub>
6.34	H	H	4-chlorophenyl	CH <sub>3</sub>
6.35	H	H	4-bromophenyl	CF <sub>3</sub>
6.36	H	H	2-thienyl	CF <sub>3</sub>
6.37	H	H	2-thienyl	CH <sub>3</sub>
6.38	H	H	3-thienyl	CF <sub>3</sub>
6.39	H	H	3-thienyl	CH <sub>3</sub>
6.40	H	H	2-furyl	CF <sub>3</sub>
6.41	H	H	3-furyl	CF <sub>3</sub>
6.42	H	H	2-pyridyl	CF <sub>3</sub>
6.43	H	H	4-pyridyl	CF <sub>3</sub>
6.44	H	H	$\alpha$ -methylcyclopropyl	CF <sub>3</sub>
6.45	H	H	$\alpha$ -methylcyclopropyl	CH <sub>3</sub>

Throughout this description, temperatures are given in degrees Celsius; "NMR" means nuclear magnetic resonance spectrum; MS stands for mass spectrum; and "%" is percent by weight, unless corresponding concentrations are indicated in other units.

The following abbreviations are used throughout this description:

m.p. = melting point

b.p.= boiling point.

s = singlet

br = broad

d = doublet

dd = doublet of doublets

t = triplet

q = quartet

m = multiplet

ppm = parts per million

Table 7 shows selected melting point and selected NMR data, all with  $\text{CDCl}_3$  as the solvent (unless otherwise stated; if a mixture of solvents is present, this is indicated as, for example, ( $\text{CDCl}_3$  /  $d_6$ -DMSO)), (no attempt is made to list all characterising data in all cases) for compounds of Tables 1 to 6. Unless otherwise stated, the data relate to a cis/trans mixture of each compound.

Table 7

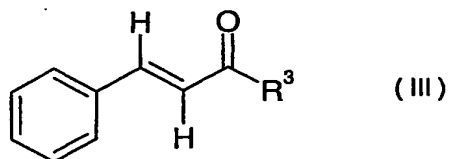
Compound Number	$^1\text{H}$ -NMR data: (ppm/multiplicity/number of Hs).	m.p. / ( $^{\circ}\text{C}$ )
1.3	0.6-0.90/m/8H(cis and trans); 1.02/d/6H(cis);1.11/6H(trans); 1.48/m/1H(trans); 1.78/m/1H(cis); 3.83/s/4H( $\text{NH}_2$ cis and trans); 6.68/m/4H(cis and trans); 7.0/m/4H(cis and trans).	oil
1.5	0.6-1.1/m/6H(cis and trans); 0.95-1.01/2d/12H(cis and trans); 1.25/m/2H(cis or trans); 1.40/m/2H(cis or trans); 1.78/m/2H(cis or trans); 3.85/s/4H( $\text{NH}_2$ cis and trans); 6.70/m/4H(cis and trans); 7.0/m/4H(cis and trans).	oil
1.6(trans)	0.52/m/1H(trans); 0.80/m/1H(trans); 0.97/s/9H(trans); 1.08/m/1H(trans); 1.57/m/1H(trans); 3.85/s/2H(trans); 6.68/m/2H(trans); 7.0/m/2H(trans).	oil
1.10		oil
1.13	0.62-1.98/m/30H(cis and trans); 3.80/s/4H(cis and trans); 6.65/m/4H(cis and trans); 6.97/m/4H(cis and trans).	oil

2.5		99-102
2.17		75-78
2.18		74-79
2.23		134- 136
2.24		110- 112
2.45	0.6-1.90/m/30H(cis and trans); 4.0/s/6H(cis and trans); 7.0-7.28/m/6H(cis and trans); 8.0/s/1H(trans); 8.05/s/1H(cis); 8.12/d/2H(trans); 8.20/d/2H(cis).	resin
2.46		113- 118
3.5		74-78
3.17		61-65
3.23		92-96
3.49	0.6-1.90/m/30H(cis and trans); 3.70/s/6H(cis and trans); 6.98-7.35/m/8H(cis and trans); 8.08/s(broad)/2H(cis and trans); 8.17/d/2H(trans); 8.25/d/2H(cis).	resin
4.10		69-74
4.12		resin
4.26		138- 142
5.5		resin
5.12		83-86
5.28		115- 119
6.10		resin

The compounds according to formula (I) may be prepared according to the following reaction schemes.

Scheme 1

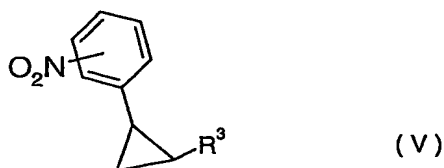
A compound of formula (II) [where  $R^3$  is as defined above for a compound of formula (I)] may be prepared by a reaction sequence starting with a crossed-aldol condensation of benzaldehyde with a ketone of formula  $CH_3C(O)R^3$  [where  $R^3$  is as defined above for a compound of formula (I)] in the presence of NaOH or KOH in a solvent (such as water or ethanol) and usually under reflux conditions or alternatively by reaction of benzaldehyde with a Wittig reagent under standard conditions. The resulting  $\alpha,\beta$ -unsaturated ketone of formula (III) [where  $R^3$  is as defined above for a compound of formula (I)]:



may then be converted into a compound of formula (IV) [where  $R^3$  is as defined above for a compound of formula (I)]:



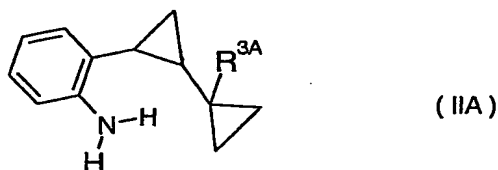
by reacting first with hydrazine hydrate in ethanol under reflux conditions and then heating (in the range 150 to 250°C) in the presence of KOH (distilling off the solvent). After nitration with  $HNO_3/H_2O$  or  $HNO_3$ /acetic anhydride in a cooled vessel (in the range -30°C to 0°C), the resultant o/p-mixture of nitrobenzene of formula (V) [where  $R^3$  is as defined above for a compound of formula (I)]:



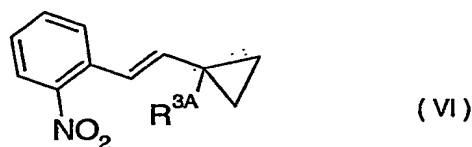
may then be separated and catalytically reduced ( $\text{Pt/C/H}_2$  or  $\text{Ra-Ni/H}_2$ ) in a solvent (such as methanol, ethanol or TMF) at room temperature, to produce a crude o/p-mixture of a compound of formula (II), which may be further purified by standard techniques.

### Scheme 2

5 The synthesis of an amine of formula (IIA)



[where  $\text{R}^{3A}$  is hydrogen or methyl] may be accomplished by a reaction sequence started by a Wittig reaction of o-nitrobenzaldehyde with a ylide [prepared from a  
 10 cyclopropylmethytriphenylphosphonium bromide in the presence of a strong base, such as NaH in a solvent such as DMSO, in the range 0-85°C. The resulting E/Z-mixture of a compound of formula (VI)



[where  $\text{R}^{3A}$  is hydrogen or methyl] may be converted to a compound of formula (VII)



by the application of the Simmons Smith reaction ( $\text{Zn/Cu, CH}_2\text{I}_2$ , ether as solvent) to the olefin group of the compound of formula (VI). The reduction of the nitro group of the corresponding compound of formula (VII) may be performed using the conditions described in Scheme 1, to produce a compound of formula (IIA).

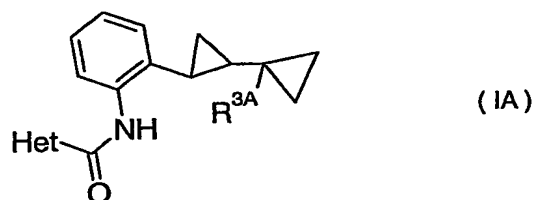
20 Scheme 3

A compound of formula (I) may be prepared by reacting a compound of formula  $\text{Het-C(=O)-R}^*$  [where  $\text{R}^*$  is halogen, hydroxy or  $\text{C}_{1-6}$  alkoxy, but preferably chloro] with a compound of formula (II) as prepared above in the presence of a base (such as

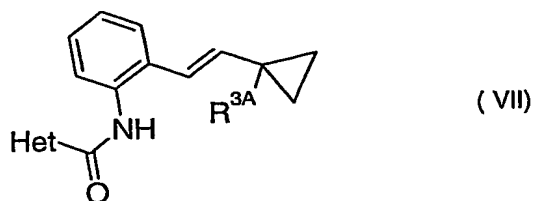
triethylamine, Hunig base, sodium bicarbonate, sodium carbonate, potassium carbonate, pyridine or quinoline, but preferably triethylamine) and in a solvent (such as diethylether, TBME, THF, dichloromethane, chloroform, DMF or NMP) for between 10minutes and 48hours (preferably 12 to 24hours) and between 0°C and reflux (preferably 20 to 25°C). When R\* is hydroxy, a coupling agent [such as benzotriazol-1-yloxytris(dimethylamino) phosphoniumhexafluorophosphate, bis-(2-oxo-3-oxazolidinyl)-phosphinic acid chloride, N,N'-dicyclohexylcarbodiimide or 1,1'-carbonyl-diimidazole] may be used.

Scheme 4

A compound of formula (IA)



[where R<sup>3A</sup> is hydrogen or methyl] may be prepared by the reduction of the nitro group of a compound of formula (VI) [where R<sup>3A</sup> is hydrogen or methyl] using standard conditions (for example, catalytic reduction or Bechamp-reduction) followed by amidation with an acid chloride to provide a compound of formula (VII) [where R<sup>3A</sup> is hydrogen or methyl]



which is subsequently used in a Simmons-Smith reaction (Zn/Cu, CH<sub>2</sub>I<sub>2</sub>, ether as solvent) to provide a compound of formula (IA).

Surprisingly, it has now been found that the novel compounds of formula (I) have, for practical purposes, a very advantageous spectrum of activities for protecting plants against diseases that are caused by fungi as well as by bacteria and viruses.

The compounds of formula (I) can be used in the agricultural sector and related fields of use as active ingredients for controlling plant pests. The novel compounds are distinguished by excellent activity at low rates of application, by being well tolerated by plants and by being environmentally safe. They have very useful curative, preventive and systemic properties and are used for protecting numerous cultivated plants. The compounds of formula I can be used to inhibit or destroy the pests that occur on plants or parts of plants (fruit, blossoms, leaves, stems, tubers, roots) of different crops of useful plants, while at the same time protecting also those parts of the plants that grow later e.g. from phytopathogenic microorganisms.

It is also possible to use compounds of formula (I) as dressing agents for the treatment of plant propagation material, in particular of seeds (fruit, tubers, grains) and plant cuttings (e.g. rice), for the protection against fungal infections as well as against phytopathogenic fungi occurring in the soil.

The compounds of formula (I) are, for example, effective against the phytopathogenic fungi of the following classes: Fungi imperfecti (e.g. Botrytis, Pyricularia, Helminthosporium, Fusarium, Septoria, Cercospora and Alternaria) and Basidiomycetes (e.g. Rhizoctonia, Hemileia, Puccinia). Additionally, they are also effective against the Ascomycetes classes (e.g. Venturia and Erysiphe, Podosphaera, Monilinia, Uncinula) and of the Oomycetes classes (e.g. Phytophthora, Pythium, Plasmopara). Outstanding activity has been observed against powdery mildew (Erysiphe spp.). Furthermore, the novel compounds of formula I are effective against phytopathogenic bacteria and viruses (e.g. against Xanthomonas spp, Pseudomonas spp, Erwinia amylovora as well as against the tobacco mosaic virus).

Within the scope of present invention, target crops to be protected typically comprise the following species of plants: cereal (wheat, barley, rye, oat, rice, maize, sorghum and related species); beet (sugar beet and fodder beet); pomes, drupes and soft fruit (apples, pears, plums, peaches, almonds, cherries, strawberries, raspberries and blackberries); leguminous plants (beans, lentils, peas, soybeans); oil plants (rape, mustard, poppy, olives, sunflowers, coconut, castor oil plants, cocoa beans, groundnuts); cucumber plants (pumpkins, cucumbers, melons); fibre plants (cotton, flax, hemp, jute); citrus fruit (oranges, lemons, grapefruit, mandarins); vegetables (spinach, lettuce, asparagus, cabbages, carrots, onions, tomatoes, potatoes, paprika); lauraceae (avocado,

cinnamomum, camphor) or plants such as tobacco, nuts, coffee, eggplants, sugar cane, tea, pepper, vines, hops, bananas and natural rubber plants, as well as ornamentals.

The compounds of formula (I) are used in unmodified form or, preferably, together with the adjuvants conventionally employed in the art of formulation. To this end they are conveniently formulated in known manner to emulsifiable concentrates, coatable pastes, directly sprayable or dilutable solutions, dilute emulsions, wettable powders, soluble powders, dusts, granulates, and also encapsulations e.g. in polymeric substances. As with the type of the compositions, the methods of application, such as spraying, atomising, dusting, scattering, coating or pouring, are chosen in accordance with the intended objectives and the prevailing circumstances. The compositions may also contain further adjuvants such as stabilizers, antifoams, viscosity regulators, binders or tackifiers as well as fertilizers, micronutrient donors or other formulations for obtaining special effects.

Suitable carriers and adjuvants can be solid or liquid and are substances useful in formulation technology, e.g. natural or regenerated mineral substances, solvents, dispersants, wetting agents, tackifiers, thickeners, binders or fertilizers. Such carriers are for example described in WO 97/33890.

The compounds of formula (I) are normally used in the form of compositions and can be applied to the crop area or plant to be treated, simultaneously or in succession with further compounds. These further compounds can be e.g. fertilizers or micronutrient donors or other preparations which influence the growth of plants. They can also be selective herbicides as well as insecticides, fungicides, bactericides, nematocides, molluscicides or mixtures of several of these preparations, if desired together with further carriers, surfactants or application promoting adjuvants customarily employed in the art of formulation.

The compounds of formula (I) can be mixed with other fungicides, resulting in some cases in unexpected synergistic activities. Mixing components which are particularly preferred are azoles, such as azaconazole, BAY 14120, bitertanol, bromuconazole, cyproconazole, difenoconazole, diniconazole, epoxiconazole, fenbuconazole, fluquinconazole, flusilazole, flutriafol, hexaconazole, imazalil, imibenconazole, ipconazole, metconazole, myclobutanil, pefurazoate, penconazole, pyrifenox, prochloraz, propiconazole, simeconazole, tebuconazole, tetraconazole, triadimefon,



triadimenol, triflumizole, triticonazole; pyrimidinyl carbinole, such as ancymidol, fenarimol, nuarimol; 2-amino-pyrimidines, such as bupirimate, dimethirimol, ethirimol; morpholines, such as dodemorph, fenpropidine, fenpropimorph, spiroxamine, tridemorph; anilinopyrimidines, such as cyprodinil, mepanipyrim, pyrimethanil;

5 pyrrroles, such as fenpiclonil, fludioxonil; phenylamides, such as benalaxyl, furalaxyl, metalaxyl, R-metalaxyl, ofurace, oxadixyl; benzimidazoles, such as benomyl, carbendazim, debacarb, fuberidazole, thiabendazole; dicarboximides, such as chlozolate, dichlozoline, iprodione, myclozoline, procymidone, vinclozoline; carboxamides, such as carboxin, fenfuram, flutolanil, mepronil, oxycarboxin,

10 thifluzamide; guanidines, such as guazatine, dodine, iminoctadine; strobilurines, such as azoxystrobin, kresoxim-methyl, metominostrobin, SSF-129, trifloxystrobin, picoxystrobin, BAS 500F (proposed name pyraclostrobin), BAS 520; dithiocarbamates, such as ferbam, mancozeb, maneb, metiram, propineb, thiram, zineb, ziram; N-halomethylthiotetrahydrophthalimides, such as captafol, captan, dichlofluanid,

15 fluoromides, folpet, tolyfluanid; Cu-compounds, such as Bordeaux mixture, copper hydroxide, copper oxychloride, copper sulfate, cuprous oxide, mancopper, oxine-copper; nitrophenol-derivatives, such as dinocap, nitrothal-isopropyl; organo-p-derivatives, such as edifenphos, iprobenphos, isoprothiolane, phosdiphen, pyrazophos, tolclofos-methyl; various others, such as acibenzolar-S-methyl, anilazine, benthiavalicarb, blasticidin-S,

20 chinomethionate, chloroneb, chlorothalonil, cyflufenamid, cymoxanil, dichlone, diclomezine, dicloran, diethofencarb, dimethomorph, SYP-LI90 (proposed name: flumorph), dithianon, ethaboxam, etridiazole, famoxadone, fenamidone, fenoxanil, fentin, ferimzone, fluazinam, flusulfamide, fenhexamid, fosetyl-aluminium, hymexazol, iprovalicarb, IKF-916 (cyazofamid), kasugamycin, methasulfocarb, metrafenone,

25 nicobifen, pencycuron, phthalide, polyoxins, probenazole, propamocarb, pyroquilon, quinoxifen, quintozene, sulfur, triazoxide, tricyclazole, triforine, validamycin, zoxamide (RH7281).

A preferred method of applying a compound of formula (I), or an agrochemical composition which contains at least one of said compounds, is foliar application. The

30 frequency of application and the rate of application will depend on the risk of infestation by the corresponding pathogen. However, the compounds of formula I can also penetrate the plant through the roots via the soil (systemic action) by drenching the locus of the

plant with a liquid formulation, or by applying the compounds in solid form to the soil, e.g. in granular form (soil application). In crops of water rice such granulates can be applied to the flooded rice field. The compounds of formula I may also be applied to seeds (coating) by impregnating the seeds or tubers either with a liquid formulation of the fungicide or coating them with a solid formulation.

A formulation [that is, a composition containing the compound of formula (I)] and, if desired, a solid or liquid adjuvant, is prepared in a known manner, typically by intimately mixing and/or grinding the compound with extenders, for example solvents, solid carriers and, optionally, surface active compounds (surfactants).

The agrochemical formulations will usually contain from 0.1 to 99% by weight, preferably from 0.1 to 95% by weight, of the compound of formula I, 99.9 to 1% by weight, preferably 99.8 to 5% by weight, of a solid or liquid adjuvant, and from 0 to 25% by weight, preferably from 0.1 to 25% by weight, of a surfactant.

Advantageous rates of application are normally from 5g to 2kg of active ingredient (a.i.) per hectare (ha), preferably from 10g to 1kg a.i./ha, most preferably from 20g to 600g a.i./ha. When used as seed drenching agent, convenient dosages are from 10mg to 1g of active substance per kg of seeds.

Whereas it is preferred to formulate commercial products as concentrates, the end user will normally use dilute formulations.

The following non-limiting Examples illustrate the above-described invention in more detail.

#### EXAMPLE 1

This Example illustrates the preparation of Compound 1.5.

To a mixture of 17.4g (0.1mol) (2-isobutyl-cyclopropyl)benzene and 80ml of acetic acid anhydride was added a solution of 6.0g (0.095mol) nitric acid and 40ml acetic acid anhydride in such a manner that the internal temperature was kept constant at  $-30^{\circ}\text{C}$ . The resulting reaction mixture was stirred for 1hour at  $-30^{\circ}\text{C}$  and then for 2hours at  $0^{\circ}\text{C}$ . Then the mixture was poured onto 500ml of ice water and extracted three times with hexane. The hexane phases were combined and twice washed with 5% aqueous bicarbonate solution. After drying of the organic phase over sodium sulphate and distilling off the solvent in a water jet vacuum, the crude reaction product was obtained. Purification by flash chromatography over silica gel (eluant: ethylacetate/hexane 1:10)

yielded 10.5g of a yellow oil (mixture of para- and ortho-nitroisomers) which was directly used in the next step. This isomeric mixture [consisting of 10.5g (0.048mol) 1-(2-isobutyl-cyclopropyl)2-nitrobenzene and 1-(2-isobutyl-cyclopropyl)-4-nitrobenzene] was dissolved in 110ml of ethanol and hydrogenated over 5%Pt/C catalyst for 45minutes. After the theoretical uptake of hydrogen had occurred, the catalyst was filtered off and the solvent was removed in vacuo. The crude isomeric aniline mixture was purified by flash chromatography (eluant: ethylacetate/hexane 1:2). 6.38g of 2-(2-isobutyl-cyclopropyl)phenyl amine was obtained as a yellow oil (cis/trans mixture). The structure was elucidated by NMR-spectroscopy (see Table 7).

#### EXAMPLE 2

This Example illustrates the preparation of Compound 3.17.

A solution of 0.35g (0.0018mol) 1-methyl-4-trifluoromethyl-pyrrole-3-carboxylic acid and 0.24g (0.0019mol) oxalylchloride in 15ml methylenechloride was stirred for 3hours at room temperature in the presence of two drops of absolute DMF. Then the acid chloride solution was slowly added to a solution of 0.34g (0.0018mol) 2-(2-isobutyl-cyclopropyl) phenylamine, 0.27g (0.0027mol) triethylamine and 10ml methylene chloride. The resulting mixture was then stirred for 16hours at room temperature. After removal of the solvent in vacuo, the crude material was taken up in ca. 100ml ethylacetate. The ethylacetate phase was twice washed with water and after drying the organic phase, the solvent was again distilled off in a water jet vacuum. The crude product was purified by flash chromatography (eluant: hexane/ethylacetate/methylene chloride 1:2:2). Yield: 0.52g 1-methyl-4-trifluoromethyl-1H-pyrrole-3-carboxylic acid [2-(2-isobutyl-cyclopropyl)phenyl]amide in the form of a white powder (cis/trans-mixture); m.p.:61-65°C.

#### FORMULATION EXAMPLES FOR COMPOUNDS OF FORMULA (I)

Working procedures for preparing formulations of the compounds of formula I such as Emulsifiable concentrates, Solutions, Granulates, Dusts and Wettable powders are described in WO 97/33890.

#### Biological Examples: Fungicidal actions

##### Example B-1: Action against *Puccinia recondita* / wheat (Brownrust on wheat)

1 week old wheat plants cv. Arina are treated with the formulated test compound (0.02% active ingredient) in a spray chamber. One day after application wheat plants are

inoculated by spraying a spore suspension ( $1 \times 10^5$  uredospores/ml) on the test plants. After an incubation period of 2 days at 20°C and 95% r. h. plants are kept in a greenhouse for 8 days at 20°C and 60% r.h. The disease incidence is assessed 10 days after inoculation.

- 5 Compounds of Tables 2, 3, 4 and 5 show good activity in this test (<20% infestation). Infestation is prevented virtually completely (0-5% infestation) with each of compounds 2.5, 2.17, 2.18, 2.23, 2.24, 2.45, 2.46, 3.5, 3.17, 3.23, 3.49, 4.10, 4.12, 4.26, 5.6 and 5.12.

Example B-2: Action against *Podosphaera leucotricha* / apple (Powdery mildew on apple)

- 10 5 week old apple seedlings cv. McIntosh are treated with the formulated test compound (0.002% active ingredient) in a spray chamber. One day after application apple plants are inoculated by shaking plants infected with apple powdery mildew above the test plants. After an incubation period of 12 days at 22°C and 60% r.h. under a light regime of 14/10 hours (light/dark) the disease incidence is assessed.

15 Compounds of Tables 2-4 show good activity in this test. The compounds 2.5, 2.17, 2.18, 2.23, 2.24, 2.45, 2.46, 3.5, 3.17, 3.23, 3.49, 4.10 and 4.12 each exhibit strong efficacy (<20% infestation).

Example B-3: Action against *Venturia inaequalis* / apple (Scab on apple)

- 20 4 week old apple seedlings cv. McIntosh are treated with the formulated test compound (0.02% active ingredient) in a spray chamber. One day after application apple plants are inoculated by spraying a spore suspension ( $4 \times 10^5$  conidia/ml) on the test plants. After an incubation period of 4 days at 21°C and 95% r.h. the plants are placed for 4 days at 21°C and 60% r.h. in a greenhouse. After another 4 day incubation period at 25 21°C and 95% r.h. the disease incidence is assessed.

Compounds of Tables 2 and 3 show good activity in this test. The compounds 2.5, 2.17, 2.18, 2.23, 2.24, 2.45, 2.46, 3.5, 3.17, 3.23 and 3.49 each exhibit strong efficacy (<20% infestation).

Example B-4: Action against *Erysiphe graminis* / barley (Powdery mildew on barley)

- 30 1 week old barley plants cv. Express are treated with the formulated test compound (0.02% active ingredient) in a spray chamber. One day after application barley plants are inoculated by shaking powdery mildew infected plants above the test plants. After an

incubation period of 6 days at 20°C / 18°C (day/night) and 60%r. h. in a greenhouse the disease incidence is assessed.

Compounds of Tables 2, 3, 4 and show good activity in this test. The compounds 2.5, 2.17, 2.18, 2.23, 2.24, 2.45, 2.46, 3.5, 3.17, 3.23, 3.49, 4.10 and 4.12 each exhibit strong efficacy (<20% infestation).

Example B-5: Action against *Botrytis cinerea* / apple (Botrytis on apple fruits)

In an apple fruit cv. Golden Delicious 3 holes are drilled and each filled with 30µl droplets of the formulated test compound (0.002% active ingredient). Two hours after application 50 µl of a spore suspension of *B. cinerea* (4x10<sup>5</sup> conidia/ml) are pipetted on the application sites. After an incubation period of 7 days at 22°C in a growth chamber the disease incidence is assessed.

Compounds of Tables 2-6 show good activity in this test. The compounds 2.5, 2.17, 2.18, 2.23, 2.24, 2.45, 2.46, 3.5, 3.17, 3.23, 3.49, 4.10, 4.12, 4.26, 5.6 and 5.12 each exhibit very strong efficacy (<10% infestation).

Example B-6: Action against *Botrytis cinerea* / grape (Botrytis on grapes)

5 week old grape seedlings cv. Gutedel are treated with the formulated test compound (0.002% active ingredient) in a spray chamber. Two days after application grape plants are inoculated by spraying a spore suspension (1x10<sup>6</sup> conidia/ml) on the test plants. After an incubation period of 4 days at 21°C and 95%r.h. in a greenhouse the disease incidence is assessed.

Compounds of Tables 2-6 show good activity in this test. The compounds 2.5, 2.17, 2.18, 2.23, 2.24, 2.45, 2.46, 3.5, 3.17, 3.23, 3.49, 4.10, 4.12, 4.26, 5.6 and 5.12 each exhibit very strong efficacy (<10% infestation).

Example B-7: Action against *Botrytis cinerea* / tomato (Botrytis on tomatoes)

25 4 week old tomato plants cv. Roter Gnom are treated with the formulated test compound (0.002% active ingredient) in a spray chamber. Two days after application tomato plants are inoculated by spraying a spore suspension (1x10<sup>5</sup> conidia/ml) on the test plants. After an incubation period of 4 days at 20°C and 95%r.h. in a growth chamber the disease incidence is assessed.

30 Compounds of Tables 2-6 show good activity in this test. The compounds 2.5, 2.17, 2.18, 2.23, 2.24, 2.45, 2.46, 3.5, 3.17, 3.23, 3.49, 4.10, 4.12, 4.26, 5.6 and 5.12 each exhibit very strong efficacy (<10% infestation).

Example B-8: Action against *Pyrenophora teres* / barley (Net blotch on barley)

1 week old barley plants cv. Express are treated with the formulated test compound (0.002% active ingredient) in a spray chamber. Two days after application barley plants are inoculated by spraying a spore suspension ( $3 \times 10^4$  conidia/ml) on the test plants. After an incubation period of 2 days at 20°C and 95%r.h. plants are kept for 2 days at 20°C and 60%r.h. in a greenhouse. The disease incidence is assessed 4 days after inoculation.

Compounds of Tables 2-6 show good activity in this test. The compounds 2.5, 2.17, 2.18, 2.23, 2.24, 2.45, 2.46, 3.5, 3.17, 3.23, 3.49, 4.10, 4.12, 4.26, 5.6 and 5.12 each exhibit very strong efficacy (<20% infestation).

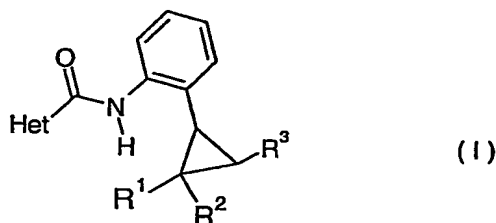
Example B-9: Action against *Septoria nodorum* / wheat (Septoria leaf spot on wheat)

1 week old wheat plants cv. Arina are treated with the formulated test compound (0.02% active ingredient) in a spray chamber. One day after application wheat plants are inoculated by spraying a spore suspension ( $5 \times 10^5$  conidia/ml) on the test plants. After an incubation period of 1 day at 20°C and 95%r.h. plants are kept for 10 days at 20°C and 60%r.h. in a greenhouse. The disease incidence is assessed 11 days after inoculation.

Compounds of Tables 2, 3 and 4 show good activity in this test. The compounds 2.5, 2.17, 2.18, 2.23, 2.24, 2.45, 2.46, 3.5, 3.17, 3.23, 3.49, 4.10 and 4.12 each exhibit strong efficacy (<20% infestation).

CLAIMS

1. A compound of formula (I):



where

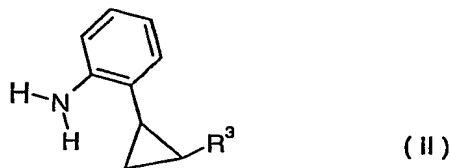
Het is a 5- or 6-membered heterocyclic ring containing one to three heteroatoms, each independently selected from oxygen, nitrogen and sulphur, the ring being substituted by groups  $R^4$ ,  $R^5$  and  $R^6$ ;

$R^1$  is hydrogen or halo;

$R^2$  is hydrogen or halo;

$R^3$  is optionally substituted  $C_{2-12}$  alkyl, optionally substituted  $C_{2-12}$  alkenyl, optionally substituted  $C_{2-12}$  alkynyl, optionally substituted  $C_{3-12}$  cycloalkyl, optionally substituted phenyl or optionally substituted heterocyclyl; and  $R^4$ ,  $R^5$  and  $R^6$  are, independently, selected from hydrogen, halo, cyano, nitro,  $C_{1-4}$  alkyl,  $C_{1-4}$  haloalkyl,  $C_{1-4}$  alkoxy( $C_{1-4}$ )alkyl and  $C_{1-4}$  haloalkoxy( $C_{1-4}$ )alkyl, provided that at least one of  $R^4$ ,  $R^5$  and  $R^6$  is not hydrogen.

2. A compound of formula (II):



where  $R^3$  is as defined in claim 1 for a compound of formula (I).

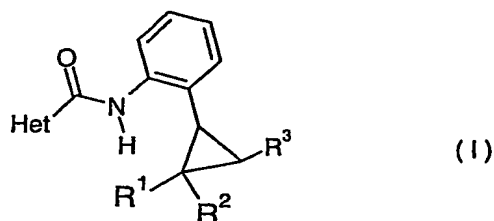
- 3 A composition for controlling microorganisms and preventing attack and infestation of plants therewith, wherein the active ingredient is a compound of formula (I) as claimed in claim 1 together with a suitable carrier.

- 4 A method of controlling or preventing infestation of cultivated plants by phytopathogenic microorganisms by application of a compound of formula (I) as claimed in claim 1 to plants, to parts thereof or the locus thereof.



ABSTRACT

A compound of formula (I):



where Het is a 5- or 6-membered heterocyclic ring containing one to three heteroatoms, each independently selected from oxygen, nitrogen and sulphur, the ring being substituted by groups  $R^4$ ,  $R^5$  and  $R^6$ ;  $R^1$  is hydrogen or halo;  $R^2$  is hydrogen or halo;  $R^3$  is optionally substituted  $C_{2-12}$  alkyl, optionally substituted  $C_{2-12}$  alkenyl, optionally substituted  $C_{2-12}$  alkynyl, optionally substituted  $C_{3-12}$  cycloalkyl, optionally substituted phenyl or optionally substituted heterocyclyl; and  $R^4$ ,  $R^5$  and  $R^6$  are, independently, selected from hydrogen, halo, cyano, nitro,  $C_{1-4}$  alkyl,  $C_{1-4}$  haloalkyl,  $C_{1-4}$  alkoxy( $C_{1-4}$ )alkyl and  $C_{1-4}$  haloalkoxy( $C_{1-4}$ )alkyl, provided that at least one of  $R^4$ ,  $R^5$  and  $R^6$  is not hydrogen. The compounds of formula (I) have plant-protective properties and are suitable for protecting plants against infestations by phytopathogenic microorganisms.

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